Journal of The Electrochemical Society, **148** (9) J45-J49 (2001)
0013-4651/2001/148(9)/J45/5/$7.00 © The Electrochemical Society, Inc.

Structure, Luminescence, and Transport Properties of $EuVO_4$

Li-Ping Li,[a,b] Guang-She Li,[c,z] Yan-Feng Xue,[a] and Hiroshi Inomata[c]

[a]*Department of Physics, Jilin University, Changchun 130023, China*
[b]*Department of Materials Science, Caltech, Pasadena, California 91125, USA*
[c]*Research Center of Supercritical Fluid Technology, Department of Chemical Engineering, Tohoku University, Sendai 980-8579, Japan*

Metastable scheelite $EuVO_4$ was stabilized by a high temperature and pressure method, which was transformed into a stable zircon phase by annealing treatment in air. Scheelite $EuVO_4$ gave strong emissions with a dominant peak at 617 nm associated with the $^5D_0$-$^7F_2$ transition of Eu^{3+}. ^{151}Eu Mössbauer spectra indicated that the isomer shift for the metastable scheelite phase was *ca*. 0.5 mm/s lower than that for the zircon phase, which was ascribed to a reduced covalency in the Eu-O bond originated via a charge transfer from oxygen to Eu^{3+} in scheelite lattice by producing an enhanced shielding of 4f electrons on the s orbital as well as a decrease in s electron density around Eu^{3+} nucleus. Impedance spectra for the zircon phase clearly demonstrated an ionic hopping in the bulk with a conductivity of *ca*. 1.0×10^{-3} S cm^{-1} at 500°C. $EuVO_4$ is proved to be both a potential phosphor and a potential ionic conductor.
 [DOI: 10.1149/1.1388633]

Manuscript received February 26, 2001. Available electronically July 30, 2001.

Oxide materials usually exhibit several novel physical phenomena under high pressures including pressure-induced ferroelectric transformations, amorphorization, and electronic transitions.[1-3] Zircon $ZrSiO_4$ exists in the earth's crust, a common accessory mineral of igneous rocks and sediments. It has excellent physical properties such as low thermal conductivity and high melting points, and shows great potential in industrial applications. It is found that zircon $ZrSiO_4$ transforms into a scheelite structure, a common feature for other zircon oxides at high pressures.[4] To well understand these pressure-induced behaviors, one has to introduce some probe ions at the framework sites to follow the microstructural variations. $REVO_4$ (RE rare earth ions, V vanadium) shows a similar crystallographic habit to $ZrSiO_4$ at high pressures with RE being framework ions. Recently, research[5-7] was carried out focusing on the phase behaviors and physical properties of $REVO_4$ at high pressures on the basis of considerations that (*i*) $REVO_4$ could become a promising host material for phosphors when some rare earth ions (such as Eu^{3+} and Tb^{3+}) were doped at RE sites. On the other hand, these dopants can also be taken as the efficient probes for identification of local structures and electronic transitions after excitation of the host and subsequent energy transfer to the dopants, and (*ii*) such studies could provide insight on the nature of phase transitions in these kinds of minerals, and furthermore, on finding new materials of different physical properties. However, there exist some controversies about both microstructural and physical properties for such materials.

With regard to the microstructures, zircon and scheelite phases are recognized to show some structural similarities. The former one has a space group of $I4_1/a$ at room temperature. Each unit cell contains four molecules, in which four equivalent rare earth ions are of D_{2d} site symmetry.[8] At high pressures, zircon $REVO_4$ transforms reversibly into a tetragonal scheelite phase that is *ca*. 10% more dense than zircon.[9] In a scheelite lattice, rare earth ions are at the sites of S_4 symmetry. However, Chen *et al.*[10] found that Eu^{3+} in scheelite $EuVO_4$ did not show the expected emission peaks from S_4 symmetry. Blin *et al.*[11] refined the structure of $Bi_{0.72}Eu_{0.28}VO_4$ in terms of scheelite and zircon structures, but found that the reliability factors are nearly the same within the experimental error.

With regard to the physical properties, scheelite phases are traditionally used for luminescence materials.[12] Esaka[13] reported that several scheelite oxides could be suitable for an oxide ion conductor, especially when the cations have similar electronegativity. This is because the scheelite phase can be considered as a double oxide of deformed fluorite type. It is well known that higher ionic conduction is closely related to the lattice expansion. As a consequence, a zircon phase could be expected to have an enhanced ionic conductivity in comparison with a scheelite phase. However, Dawson[14] pointed out that all zircon minerals are nonconductors.

It should be noted that the scheelite phase $REVO_4$ is not stable; it has a possibility to transform into some denser phases at much higher pressures.[15] But its structural behavior under annealing still remains unclear. Therefore, the controversies mentioned above probably arise from the unsolved structural stability and ionic conductivity for $REVO_4$. It appears very important to stabilize high pressure scheelite phase and to determine the phase transition in scheelite phase and ionic conduction in zircon phase. Recently, we stabilized Eu^{3+} and Tb^{3+} in ceria lattice by high temperature and pressure.[16] In this paper, we extend this method to get metastable scheelite $EuVO_4$, and furthermore, to examine the possibilities of $EuVO_4$ being both phosphors and ionic conductors.

Experimental

Analytical grade reagent (AR) Eu_2O_3, and V_2O_5 AR were used as the starting materials. They were weighed according to the molar ratio of Eu:V = 1. After thoroughly grinding, the mixtures were preheated at 700°C for 2 h at ambient pressure to remove completely the carbonate species absorbed on the sample surface. The mixture was put into a high pressure chamber for a belt-type apparatus as illustrated in Ref. 17. The pressure was loaded to 3.9 GPa and then the temperature was increased gradually to 700 or 900°C. After being kept at high temperature and pressure for 30 min, the specimens were quenched to room temperature under high pressure. Finally, the pressure was released and the pellet samples A (700°C) and B (900°C) were obtained. To get the stable form of the sample, we annealed sample A at 600°C in air for 2 h, and sample C was obtained.

Powder X-ray diffraction (XRD) patterns for the samples were collected at room temperature on a Rigaku 12 kW copper rotating anode X-ray diffractometer. The scan rate was 0.3° 2θ/min. The lattice parameters for the samples were calculated by the least-squares methods.

Luminescence spectra for the samples under an excitation of 488 mm were recorded using a J-YT64000 spectrometer with an Ar^+ ion laser.

^{151}Eu Mössbauer spectra of the $EuVO_4$ samples were recorded at room temperature on an Oxford MS-500 constant acceleration spectrometer. The velocity was calibrated with an α-Fe foil. The radiation source was ^{151}Eu/SmF^3. The thickness of the absorber used in the measurements was *ca*. 6-15 Eu mg/cm^2. The experimental Mössbauer data were fitted by superimposing Lorentzians.

[z] E-mail: guangshe@scf.che.tohoku.ac.jp

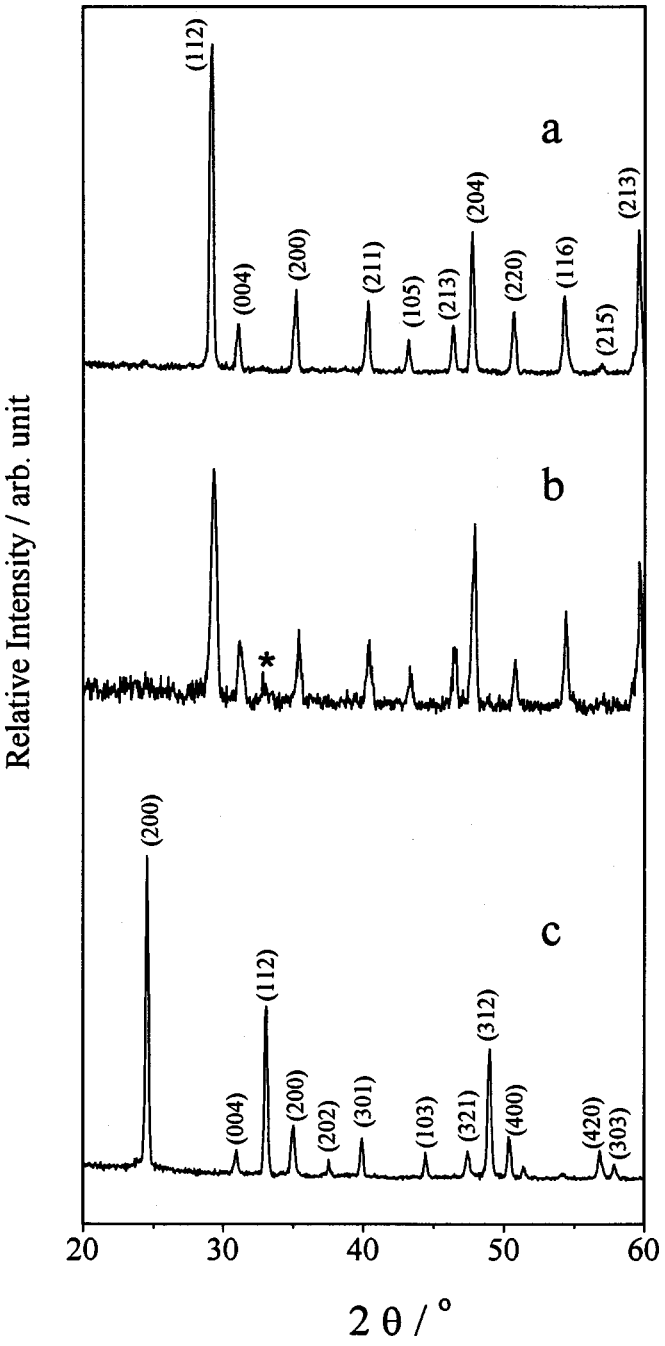

Figure 1. XRD patterns for (a) sample A prepared by high temperature (700°C) and pressure (3.9 GPa), (b) sample B at 900°C and 3.9 GPa, and (c) sample C by annealing sample A at 600°C for 2 h in air. * denotes impurity phase of $Eu^{3+}VO_3$.

The ionic conduction was determined by ac impedance technique. The opposite sides of the pellet samples were coated with silver paste and then heated at 600°C for 1/2 h to remove the organic components in the paste. The ionic conductivity for the pellet samples was measured using Solarton 1260 impedance/gain-phase analyzer with the alternating current having a frequency between 5 Hz and 13 MHz at an amplitude of 50 mV in the temperature range of 350-750°C in air.

Results and Discussion

Stabilization and thermal behavior of scheelite $EuVO_4$.—XRD pattern for sample A is shown in Fig. 1a. It is clear that high temperature (700°C) and pressure (3.9 GPa) reactions yielded a single phase sample. The diffraction data are consisted of single peaks with high symmetry, matching well with the standard diffraction data for scheelite structure (JCPDS 41-1431). No diffraction peaks were detected for the component oxides such as Eu_2O_3, V_2O_5, or $EuVO_3$. Therefore, the XRD data in Fig. 1a could be indexed in terms of a tetragonal scheelite phase with a space group of $I4_1/a$. The lattice parameters were refined as: $a = 0.5100(2)$ and $c = 1.149(3)$ nm.

Figure 1b shows the XRD pattern of sample B that is obtained at 900°C and 3.9 GPa. It can be seen that sample B is a mixture of scheelite $EuVO_4$ and traces of perovskite $EuVO_3$. As confirmed by the following Mössbauer spectra and our previous results,[16] Eu ions are present primarily in trivalent state at high temperature and pressure. Therefore, the phase separation observed from Fig. 1b was probably due to a reduction process from V^{5+} to V^{3+} under high temperature and pressure. This result is clearly different from that of $REVO_4$ at high pressure.[5] In the latter case, scheelite phase transforms to a monoclinic or $KAlF_4$ structure by packing of polyhedra.

The thermal behavior of scheelite $EuVO_4$ was studied by annealing treatment. Figure 1c gives XRD pattern of sample C that was obtained after annealing sample A in air at 600°C at ambient pressure for 2 h. The diffraction data did not contain any peaks from sample A in Fig. 1a, but instead were well coincided with those of zircon $EuVO_4$ (JCPDS 17-0260). This result indicated that scheelite $EuVO_4$ was a metastable phase and transformed into a stable tetragonal zircon structure with a space group of $I4_1/amn$ after annealing. The lattice parameters were determined to be $a = 0.7249(3)$ and $c = 0.6379(4)$ nm, which were slightly larger than the literature data: $a = 0.72373(2)$ and $c = 0.63661(3)$ nm for zircon $EuVO_4$.[8] The slight lattice expansion could be due to the local lattice distortion during the pressure releasing.

Chen *et al.*[10] reported that $EuVO_4$ sample at 4.5 GPa is a mixture of zircon and scheelite phases, single scheelite structure appeared only at a pressure as high as 5.6 GPa. Stubican *et al.*[9] found that zircon $EuVO_4$ changes into scheelite phase at 430-500°C and 5.5 GPa. In combination with the present synthetic conditions (700°C and 3.9 GPa) for single phase scheelite $EuVO_4$, it is concluded that the pressure for stabilization of scheelite phase $EuVO_4$ could be much reduced with increasing temperature. The stabilization of metastable scheelite $EuVO_4$ was probably due to the quick quenching process of high temperature and pressure reactions, and an enhanced internal stress. The effect from the latter case could be proved by introducing a larger dopant at Eu sites of scheelite $EuVO_4$ according to the fact that larger dopants could produce an increased internal stress in lattice. Indeed, Lorriaux *et al.*[18] obtained scheelite phase of $Eu_{1-x}Bi_xVO_4$, where Bi^{3+} has an ionic size much larger than that of Eu^{3+}.

Luminescence property of scheelite $EuVO_4$.—For zircon $EuVO_4$, Eu ions occupied the lattice sites of D_{2d} symmetry. Group theory predicts four luminescence peaks, two from $^5D_0$-$^7F_1$ and two from $^5D_0$-$^7F_2$ transitions. A degeneracy of the levels for $^7F_1$ leads to one emission peak. Therefore, three peaks could be observed. This has been confirmed experimentally.[10]

The emission spectrum for sample A is shown in Fig. 2. Five emission bands with a predominant peak at 617 nm were observed and could be assigned to $^5D_0$-$^7F_2$ and $^5D_0$-$^7F_1$ transitions for Eu^{3+}, respectively. $^5D_0$-$^7F_2$ emission line was composed of three components at 606, 613, and 617 nm, which is associated with the lowered local site symmetry of Eu^{3+}.[19] $^5D_0$-$^7F_1$ emission was characterized by both bands at 591 and 595 nm. These split peaks were due to the spin-orbit split ground states and crystal field splitting.[20] The dominant emission at 617 nm is typical of Eu^{3+} occupying the sites with no inversion symmetry.[21] Scheelite phase $EuVO_4$ has a tetragonal lattice, in which Eu^{3+} occupies the sites of S_4 symmetry. Group theory predicts five luminescence peaks: two $^5D_0$-$^7F_1$ and three $^5D_0$-$^7F_2$ transitions. Consistence of the present experimental results

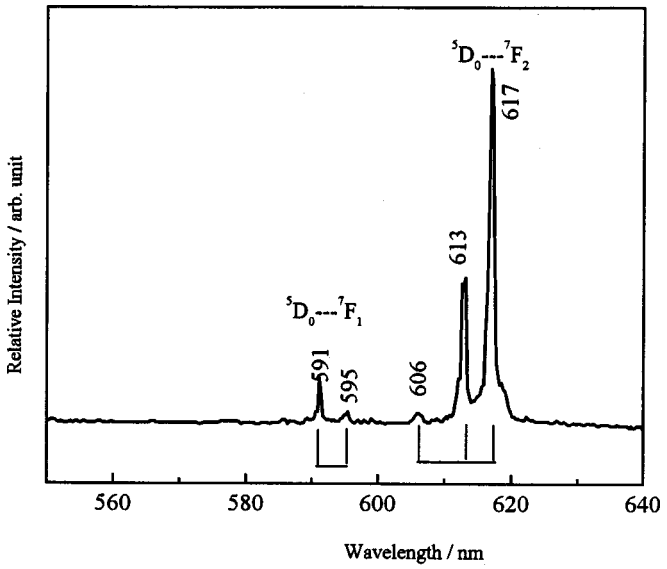

Figure 2. Emission spectrum of sample A under an excitation line of 488 nm.

and theoretical predictions indicated that Eu^{3+} is of S_4 symmetry and that the scheelite phase has a much smaller lattice distortion. The latter one is further confirmed by following Mössbauer spectroscopy. The relatively weak emission peaks at 595 and 613 nm in Fig. 2 reflected some structural similarities between scheelite and zircon $EuVO_4$.

Hyperfine parameters of $EuVO_4$ in both scheelite and zircon phases.—Mössbauer spectra for both samples A and C recorded at room temperature are shown in Fig. 3. Only single absorption lines were observed at *ca* 0 mm/s for the experimental spectra of both samples, which indicated that Eu ions were present in trivalent state in both phases. Both experimental spectra in Fig. 3 exhibited slightly asymmetric lines, which were more broadened in comparison with that of natural single line. These facts confirmed that there was an unresolved quadrupole interaction. Therefore, the experimental data could be fitted using twelve transition lines.[16] For sample A in a scheelite phase, as shown in Fig. 3a, the ^{151}Eu Mössbauer spectrum showed a broader linewidth at lower velocity than that at higher velocity. Therefore, a negative quadrupole splitting (QS) was employed for refinement of the hyperfine parameters. The difference between the experimental and fitting spectra is illustrated at the bottom of Fig. 3a. The hyperfine parameters for both phases are listed in Table I. The isomer shift (IS) for Eu^{3+} in scheelite lattice was -0.55 mm/s (referring to α-Fe), while that for sample B in the zircon phase was around 0.0 mm/s. The difference of isomer shift for both samples was *ca*. 0.5 mm/s. By contrast, the QS for scheelite $EuVO_4$ was *ca*. -8.0 mm/s, which is slightly larger than that for zircon phase.

It is known that the isomer shift is associated with the electron density around the Eu nucleus. Many factors including valence state and coordination number of Eu ions as well as Eu-O bonding characteristics have some influences on the electron density and isomer shift. Although scheelite and zircon phases of $EuVO_4$ have different space groups with Eu^{3+} being of different symmetry, the coordination number of Eu ions is the same of eight-fold. That is to say, each Eu^{3+} coordinates with eight VO_4 pyramids, the coordination number could not be the essential reason for the difference of isomer shift. Previous studies showed that Eu ions in most of Eu containing compounds are either trivalent or divalent, and in some metallic compounds it exhibits an intermediate valence state.[22] For Eu containing oxides, Eu-O bonding is covalency in nature and Eu ions could not be in an intermediate valence state. Recently first-order

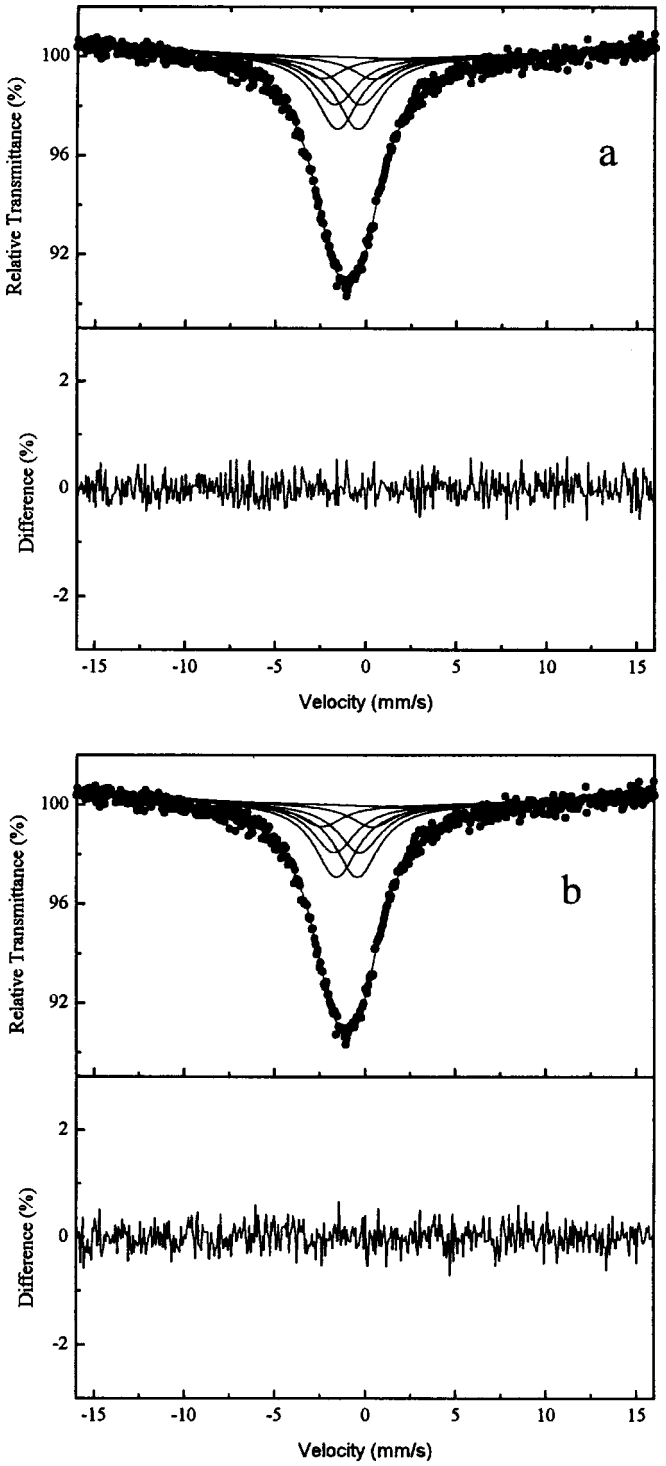

Figure 3. Mössbauer spectra for (a) samples A and (b) sample B.

Table I. Hyperfine parameters for $EuVO_4$ in scheelite and zircon structures. (Note: IS is isomer shift, QS is quadrupole splitting, and η refers to half-height width.)

Sample name	Structure type	IS (mm/s)	QS (mm/s)	η (mm/s)
A	Scheelite	-0.55 ± 0.01	-8.0 ± 0.3	0.99 ± 0.06
C	Zircon	-0.06 ± 0.02	-8.6 ± 0.3	0.99 ± 0.06

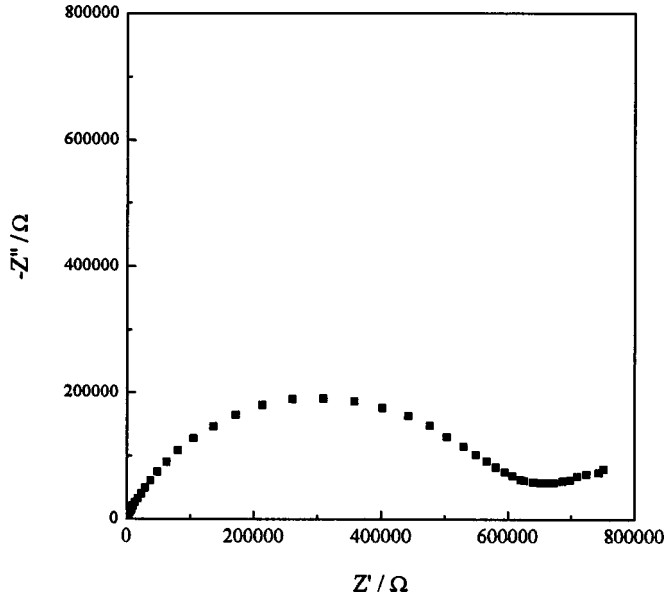

Figure 4. A typical impedance spectrum for sample C recorded at 350°C on heating.

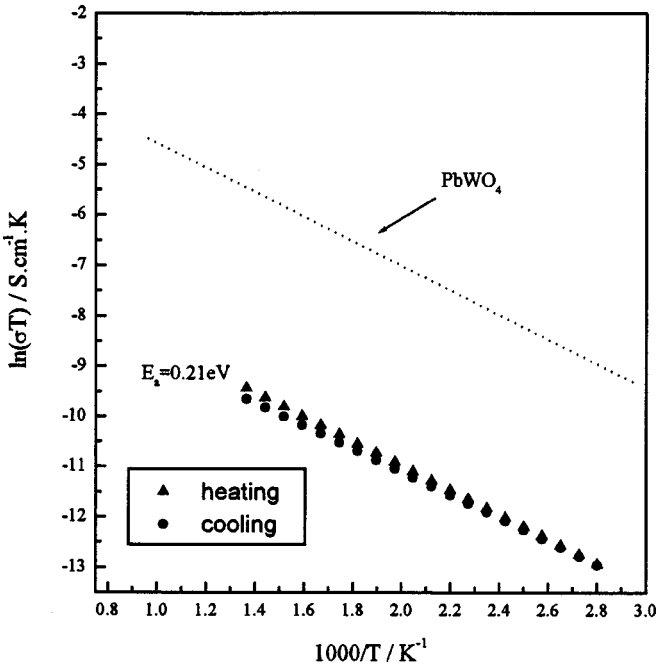

Figure 5. Temperature dependence of the conductivity for sample C.

valence averaging phase transition has been reported for several Eu containing materials,[23] *i.e.*, a charge transfer from oxygen to Eu ions may occur. For the present work, a reduced covalency in the Eu-O bond originated via charge transfer from oxygen to Eu^{3+} in scheelite $EuVO_4$ would result in an increase in the shielding effect of 4f electrons on the s orbital by decreasing s electron density at the Eu nucleus. This is probably the main reason for the small difference in isomer shift observed for scheelite and zircon $EuVO_4$. Similarly, a charge transfer from oxygen to rare earth ions[6] is used to explain the shift of absorption edge to lower energy as YVO_4 transforms from zircon to scheelite under pressures.

The fitting results of Mössbauer data in Fig. 3 for samples A and C showed a negative quadrupole interaction (see Table I). It is known that the QS is in proportion to the principal of electric field gradient, V_{zz}. Because of the ground state of Eu^{3+} being $^7F_0$, the main contribution to V_{zz} should come from the lattice contribution and the second order 4f contribution,[24] while the lattice contribution is negative. It is clear from the hyperfine parameters in Table I that the contribution of the lattice to V_{zz} for $EuVO_4$ in scheelite and zircon phases could be larger than the second order 4f contribution. The isolate value of QS for scheelite was slightly smaller than that for zircon, indicating a smaller local lattice distortion for scheelite $EuVO_4$, which is in agreement with our luminescence analysis.

Transport property of zircon $EuVO_4$.—In the section on stabilization and thermal behavior of sheelite $EuVO_4$, we showed that scheelite and zircon $EuVO_4$ could give luminescence emission. In the Abstract, we also mentioned that zircon and scheelite lattices have some structural similarities to the fluorite phase, while the latter one is a host material for ionic conductors. To examine the possibility of $EuVO_4$ being phosphor and ionic conductor, here we measured the ionic conductivity in $EuVO_4$.

Before impedance measurements, pellet sample A in the scheelite phase has to be heated at 600°C (see the Experimental section), which would lead to phase transition to zircon phase (sample C). A typical impedance spectrum for sample C at 350°C on heating is shown in Fig. 4. Only one semicircle was observed, which was primarily due to the bulk conduction. No grain boundary effect was observed. The semiarc at lower frequencies was ascribed to the electrode effect, namely, an oxygen exchange process occurring between sample and electrode. According to the structural model for mineral $ZrSiO_4$,[4] the zircon $EuVO_4$ lattice could be described as a chain of alternating edge-sharing VO_4 tetrahedra and EuO_8 triangular dodecahedra extending parallel to the *c* axis. These chains are jointed alternatively by edge sharing EuO_8 dodecahedra. Therefore, there are no intrinsic oxygen vacancies in the zircon lattice, but the oxide ions might move in the interstitial sites between the chains along *c* axis. The interstitial sites could be closely related to the local lattice distortion in the zircon phase as is indicated by the hyperfine parameters in Table I. The ionic conductivity for the bulk is determined by intersection of the corresponding semicircle on the real part of the impedance axis. The temperature dependence of conductivity for sample C is shown in Fig. 5. For comparison, the conductivity data for scheelite $PbWO_4$ in Ref. 13 are also shown. With increasing temperature, the bulk conductivity for zircon $EuVO_4$ increased linearly, which followed exactly the Arrhenius relationship. At 500°C, the conductivity was *ca.* $\sigma = 1.0 \times 10^{-3}$ S cm^{-1}, which was compatible to those of fluorite-based ionic conductors $Ce_{0.5}Bi_{0.5}O_{2-y}$ and $Ce_{0.8}Nd_{0.2}O_{2-y}$.[25,26] From Fig. 5, it is seen that all conductivity data for zircon $EuVO_4$ were lower than those of typical scheelite $PbWO_4$. This is probably related to the electronegativity difference between the framework ions. The electronegativity difference between Eu^{3+} and V^{5+} is 0.43, which is larger than 0.03 for $PbWO_4$ but much smaller than 1.36 for an oxy salt of scheelite $CaWO_4$. The small electronegativity difference could lead to a deformed fluorite-type structure with cations being at equivalence sites in lattice, accounting for a high oxide ionic conductivity.[13] The activation energy is estimated from the slope of conductivity data in Fig. 5. It is noted that activation energy for zircon $EuVO_4$ was as low as *ca.* 0.21 eV, very similar to that for $PbWO_4$, which indicated a similar local coordination state. This is consistent with our luminescence analysis above. Further doping aliovalent ions with a larger electronegativity at Eu^{3+} sites is expected to produce new ionic conductors with relatively high conductivity and moderate activation energy, which is now in progress.

Conclusions

This paper reports on the stabilization of single phase scheelite $EuVO_4$ by high temperature (700°C) and pressure (3.9 GPa). Slightly increasing the temperature to 900°C led to a phase separa-

tion accompanied by a reduction of V^{5+} to V^{3+}. Scheelite $EuVO_4$ was a metastable phase, which transformed into its stable form of zircon phase by annealing treatment. Mössbauer spectra showed that isomer shift for Eu^{3+} in scheelite lattice was lower, while the corresponding QS value was larger than those in zircon phase. Scheelite $EuVO_4$ gave a relatively strong emission. Zircon $EuVO_4$ showed a promising oxide ionic conduction in bulk such as $\sigma_{500°C} = 1.0 \times 10^{-3}$ S cm^{-1} and $E_a = 0.21$ eV, which is completely opposite to that predicted by Dawson.[14]

Acknowledgments

This work was financially supported by a fund of NSFC (no. 19804005) (L.L.)

The Japanese Ministry of Education, Sceince, Sports, and Culture assisted in meeting the publication costs of this article.

References

1. D. Gourdain, E. Moya, J. C. Chervin, B. Canny, and Ph. Pruzan, *Phys. Rev. B*, **52**, 3108 (1995).
2. A. Jayaraman, K. A. G. Schneidner, and L. Eyring, *Handbook on the Physics and Chemistry of Rare Earth*, North-Holland, Amsterdam, 1978, p. 707.
3. N. Binggeli, N. R. Kestar, and R. Chelikowsky, *Phys. Rev. B*, **49**, 3075 (1994).
4. J. C. Nipko and C. K. Loong, *Physica B*, **241-243**, 415 (1998).
5. A. Jayaraman, G. A. Kourouklis, G. P. Espinosa, A. S. Cooper, and L. G. Vanuitert, *J. Phys. Chem. Solids*, **48**, 755 (1987).
6. S. J. Duclos, A. Jayaraman, G. P. Espinosa, A. S. Cooper, and R. G. Sr. Maines, *J. Phys. Chem. Solids*, **50**, 769 (1989).
7. J. W. Hur, H. C. Lee, M. S. Jang, D. H. Yoo, and H. K. Kim, *Ferroelectrics*, **109**, 197 (1990).
8. R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Vol. 3, Interscience, New York (1965).
9. V. S. Stubican and R. Roy, *J. Appl. Phys.*, **34**, 188 (1963).
10. G. Chen, R. G. Haire, J. R. Peterson, and M. M. Abraham, *J. Phys. Chem. Solids*, **55**, 313 (1994).
11. J. L. Blin, A. Lorroaux-Rubbens, F. Wallart, and J. P. Wignacourt, *J. Mater. Chem.*, **6**, 385 (1996).
12. A. T. Aldred, *Acta Crystallogr., Sect. B: Struct. Sci.*, **40**, 569 (1984).
13. T. Esaka, *Solid State Ionics*, **136-136**, 1 (2000).
14. N. P. Dawson, *Symp. Ser. -S. Afr. Inst. Min. Metall.*, **S17**, 105 (1997).
15. A. Jayaraman, B. Batlogg, and L. G. VanUitert, *Phys. Rev. B*, **31**, 5423 (1985).
16. L. Li, G. Li, Y. Che, and W. Su, *Chem. Mater.*, **12**, 2567 (2000).
17. S. Feng, G. Li, L. Li, and X. Li, *Rev. High Pressure Sci. Technol.*, **7**, 1362 (1998).
18. R. A. Lorriaux, J. Corset, J. Ghamri, and H. Baussart, *Adv. Mater. Res.*, **1-2**, 433 (1994).
19. B. N. Mahalley, R. B. Pode, and P. K. Gupta, *Phys. Status Solidi A*, **177**, 293 (1999).
20. K. Riwotzki and M. Haase, *J. Phys. Chem. B*, **102**, 10129 (1998).
21. W. Park, R. Y. Lee, C. J. Summers, Y. R. Do, and H. G. Yang, *Mater. Sci. Eng., B*, **78**, 28 (2000).
22. I. Nowik, *Hyperfine Interact.*, **13**, 83 (1989).
23. I. Nowik, R. H. Herber, I. Felner, K. V. Ramanujachary, J. E. Sunstrom, I. Fawcett, P. Shuk, M. Greenblatt, and M. Croft, *Phys. Rev. B*, **59**, 8732 (1999).
24. C. L. Chien and A. W. Sleight, *Phys. Rev. B*, **18**, 2031 (1978).
25. G. Li, Y. Mao, L. Li, S. Feng, M. Wang, and X. Yao, *Chem. Mater.*, **11**, 1259 (1999).
26. X. Lin, L. Li, G. Li, and W. Su, *Mater. Chem. Phys.*, **69**, 236 (2001).